



# High Energy Lithium Batteries for PHEV Applications

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**Project ID: ES211**

*This presentation does not contain any proprietary, confidential, or  
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# Program Overview

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## Time line

Start Date: October 2013

End Date: March 2016

Status: Completed

## Barriers

- Meeting PHEV power specifications
- Loss of power with cycling
- Cycle and calendar life

## Partners



## Budget

Total Project Funding:

\$ 3,785,088

Cost Share:

\$ 757,018

Funding Received:

\$ 1,433,992 (Envia)

## Project Lead



# Outline

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## ☐ Overview & Objectives

## ☐ Motivation & Roadmap

## ☐ Materials Engineering

- Compositional Engineering
- Surface Engineering

## ☐ Diagnostic Studies

- Structure
- Interphase/Interface
- Electrochemical

## ☐ Theoretical Modeling

## ☐ Cell Engineering

## ☐ Conclusions & Acknowledgements

# Project Objectives - Relevance

## Goals

Develop a high capacity cathode, and Si-SiO<sub>x</sub>-C based anode and integrate them and build high capacity (0.25-40 Ah) pouch cells that exceed the ABR minimum target goals for PHEVs

## Relevance

- Identifying the root cause and solving the DC-Resistance rise at low SOC's, enabling the use of the high-energy offered by HCMR™ Li-rich cathode materials

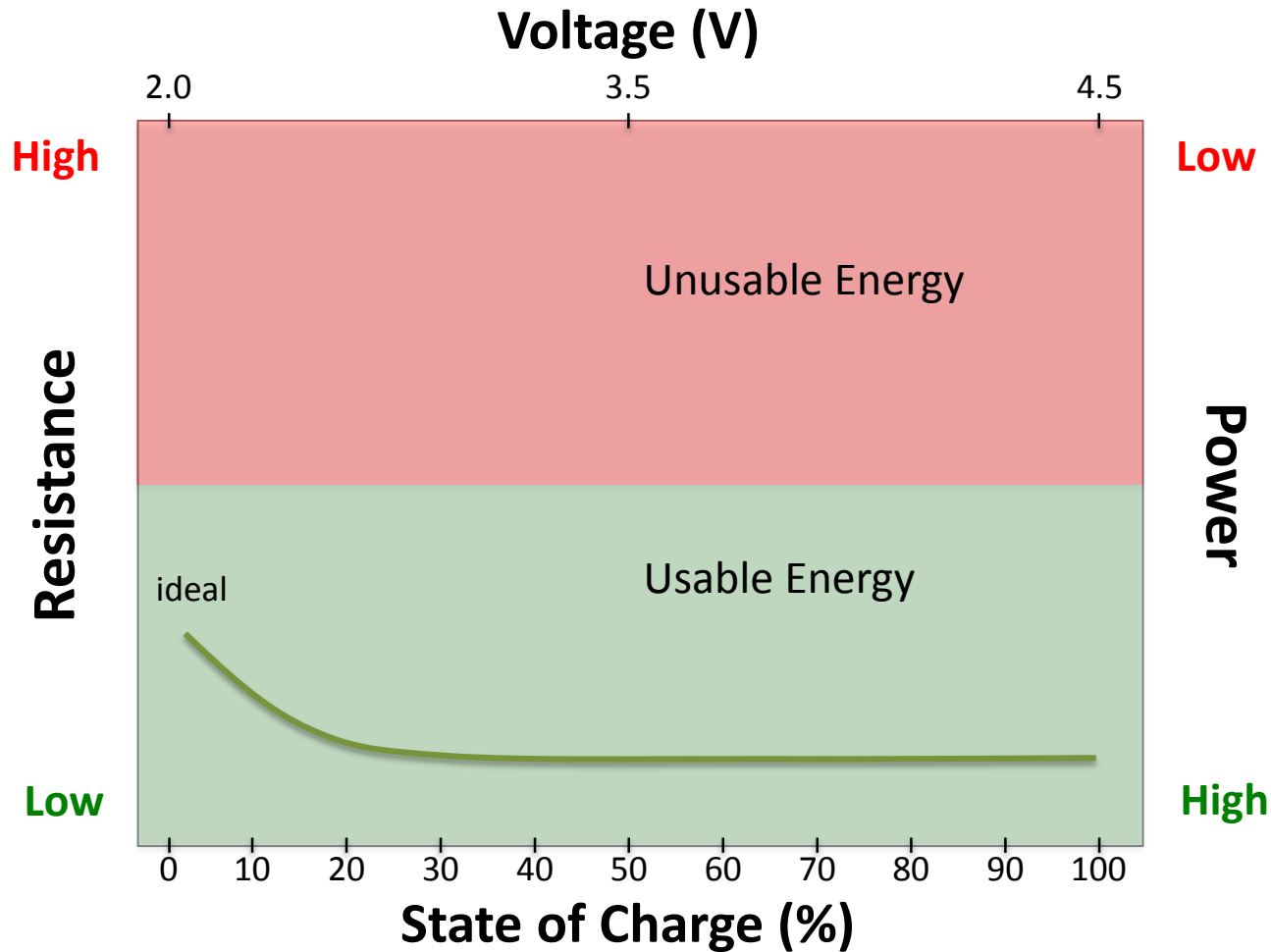
## Project Tasks

- Material development
- Nanocoating engineering
- Atomistic and cell-level modeling
- Material scale-up
- Large cell development
- Large cell testing

## Cell Targets

Characteristics	Unit	PHEV40
Specific Discharge Pulse Power	W/kg	800
Discharge Pulse Power Density	W/L	1600
Specific Regen Pulse Power	W/kg	430
Regen Pulse Power Density	W/L	860
Recharge Rate	NA	C/3
Specific Energy	Wh/kg	200
Energy Density	Wh/L	400
Calendar Life	Years	10+
Cycle Life (at 30° C with C/3 Charge and 1C Discharge rates)	Cycles	5000
Operating Temperature Range	°C	-30 to +52

# Importance of Cell DC-R/Power for Automotive Range

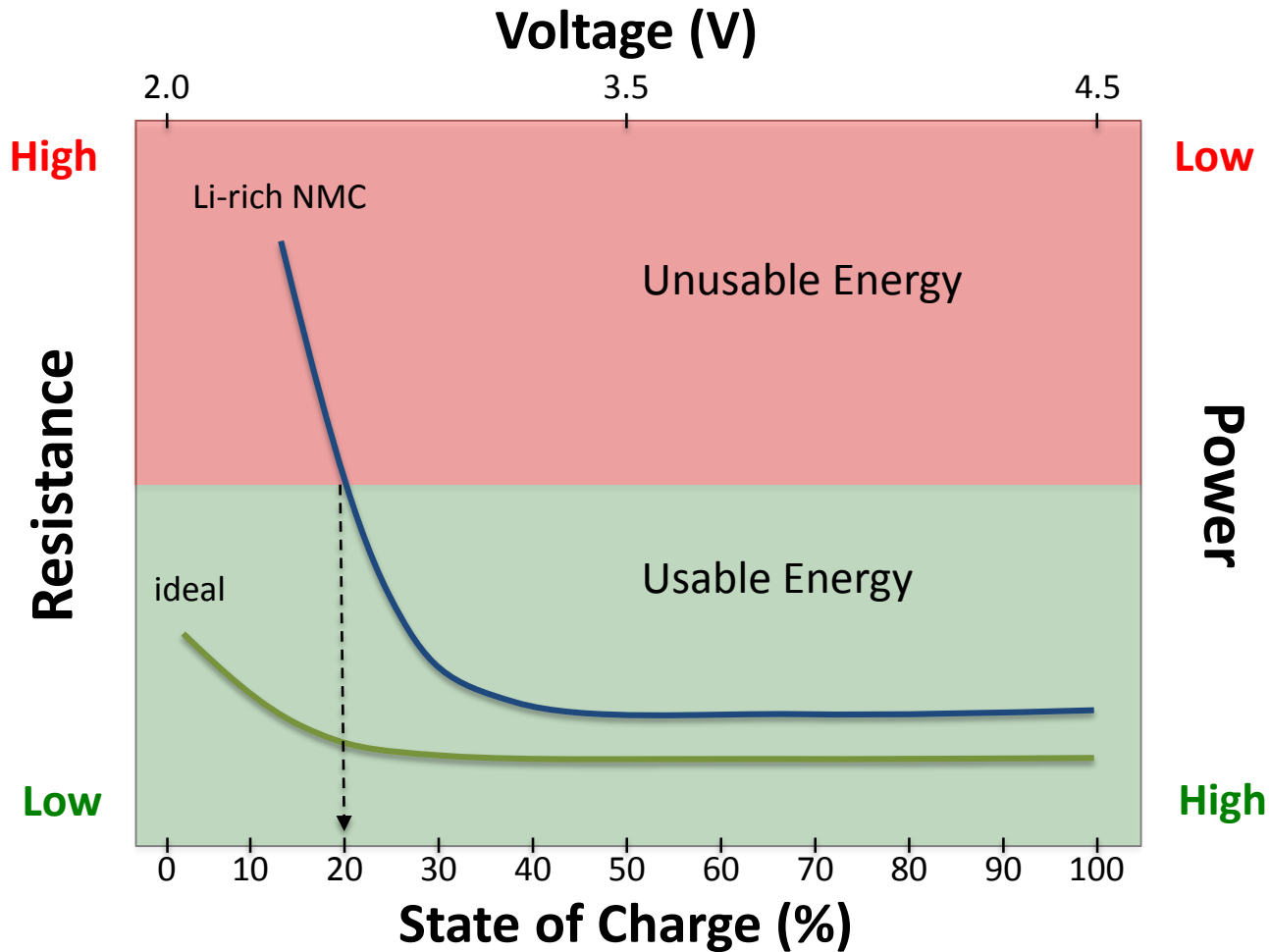


Range/Miles per charge



300 miles

# Importance of Cell DC-R/Power for Automotive Range



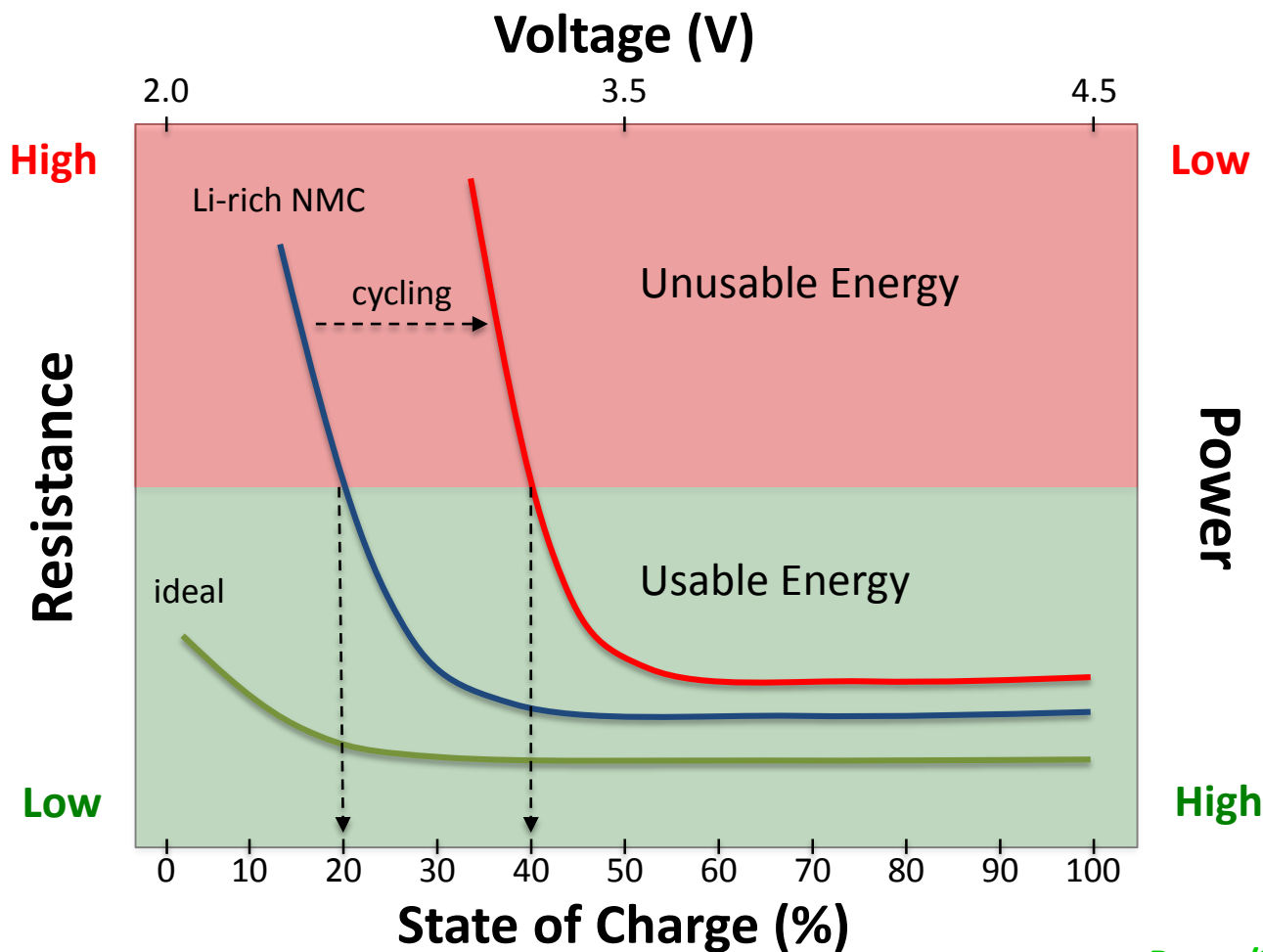
Range/Miles per charge



240 miles (-20%)

300 miles

# Importance of Cell DC-R/Power for Automotive Range



Range/Miles per charge



180 miles (-40%)



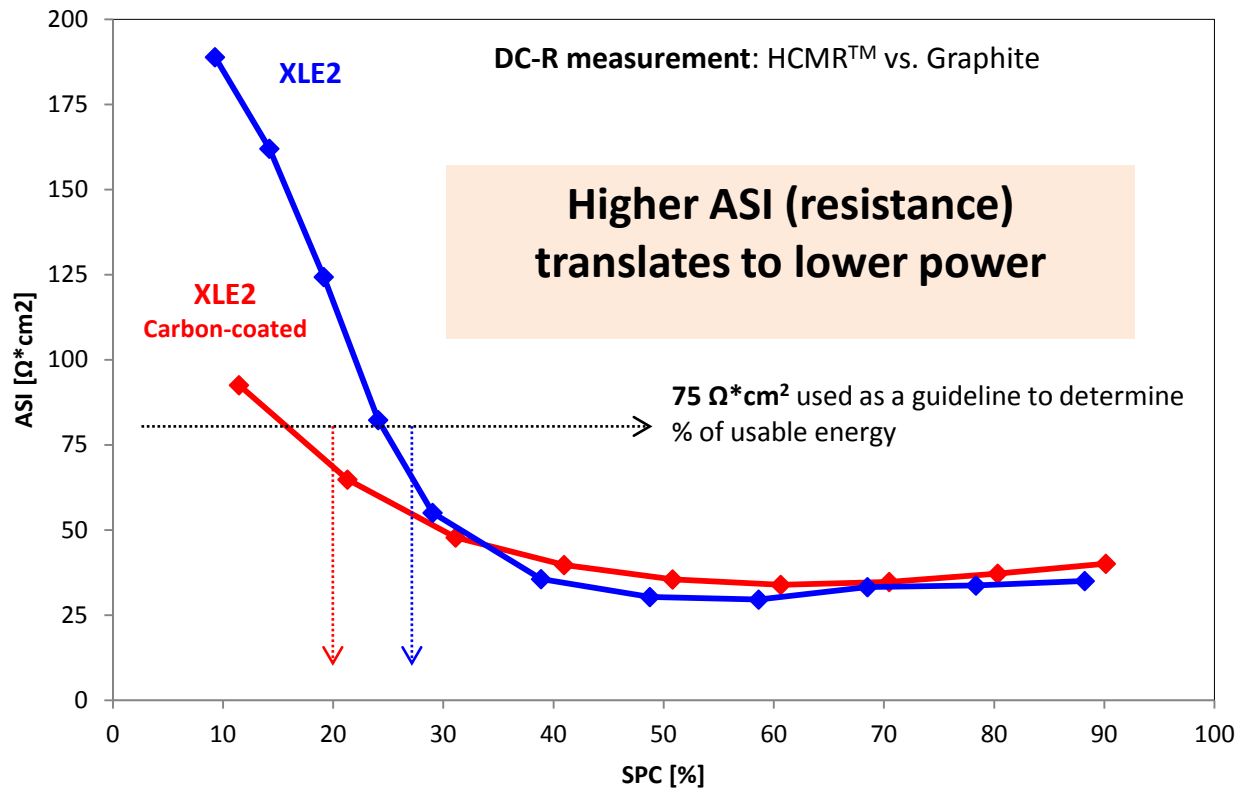
240 miles (-20%)



300 miles



# Motivation: Reduction of DC-R by Surface Coatings



- HCMR™-XLE2 material has only ~75% energy extracted from lower resistance regions
- Nevertheless, the same chemistry with a carbon-coating increases usable energy from ~75% to >82%

It is possible to increase usable energy by engineering surface coating chemistries and processes!

# Project Development Roadmap

## Atomistic modeling

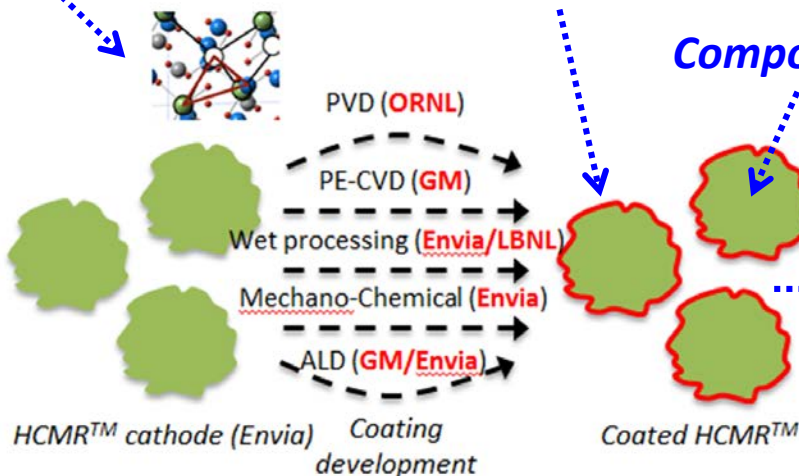
## Nanocoating

## Composition

## Challenges:

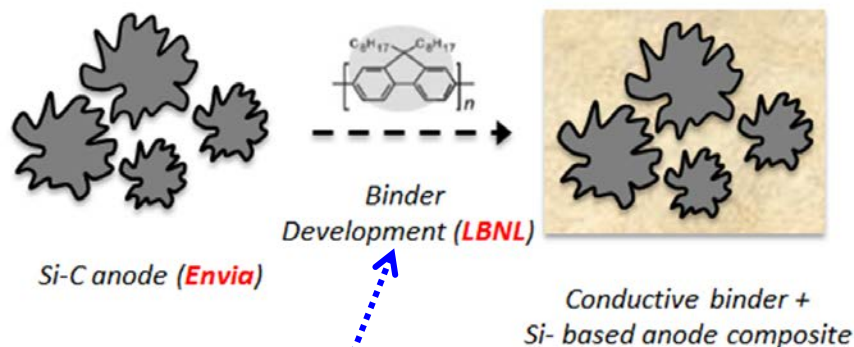
- High resistance at beginning of life  
→ **Lower power**
- Resistance growth with cycling  
→ **Loss of power**

## Cathode Development



## Diagnostic studies

## Anode Development



## Anode binder

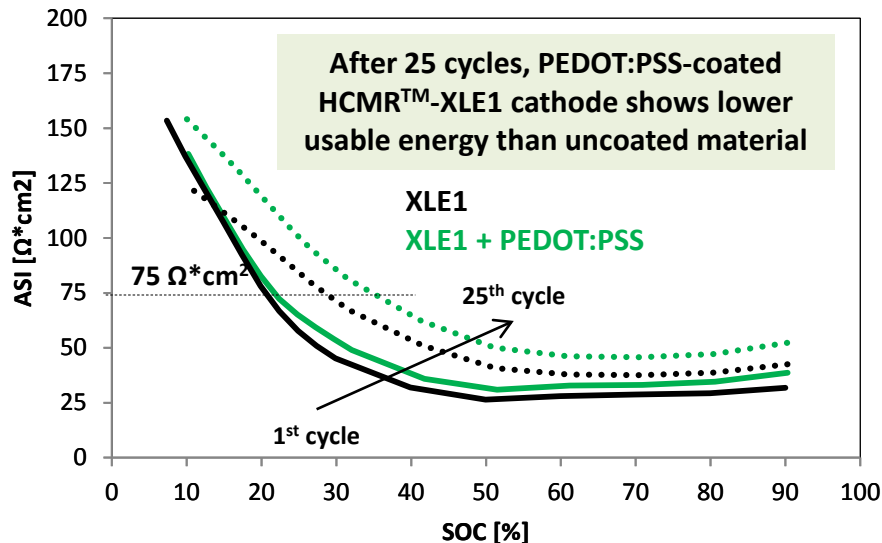
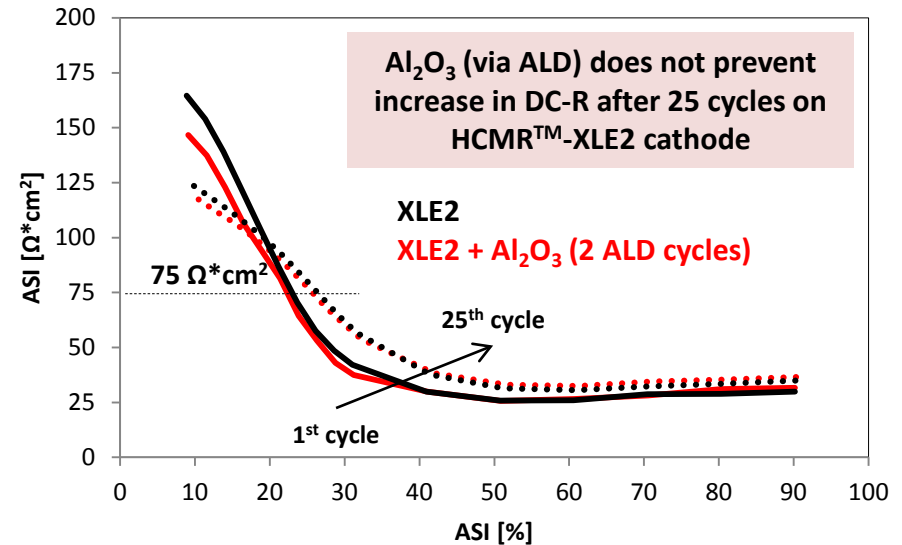
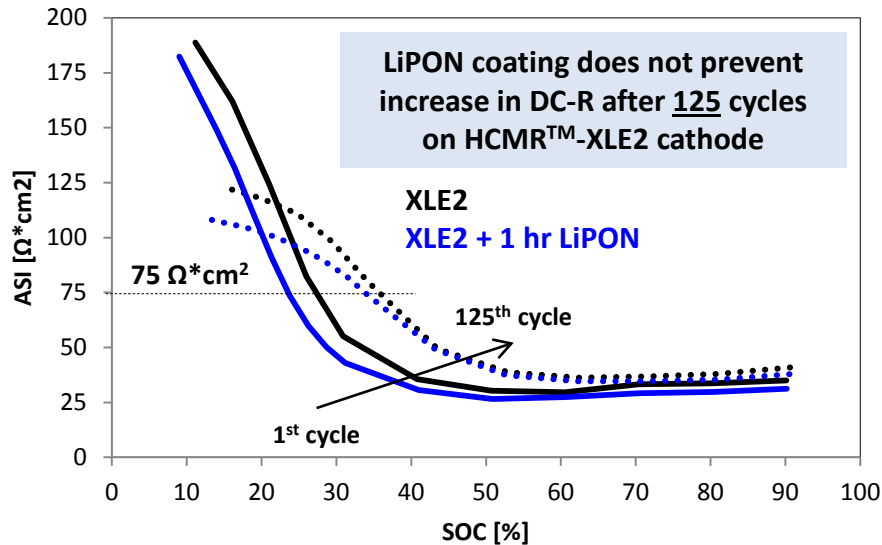
## Cell-level modeling



# Project Tasks & Timeline

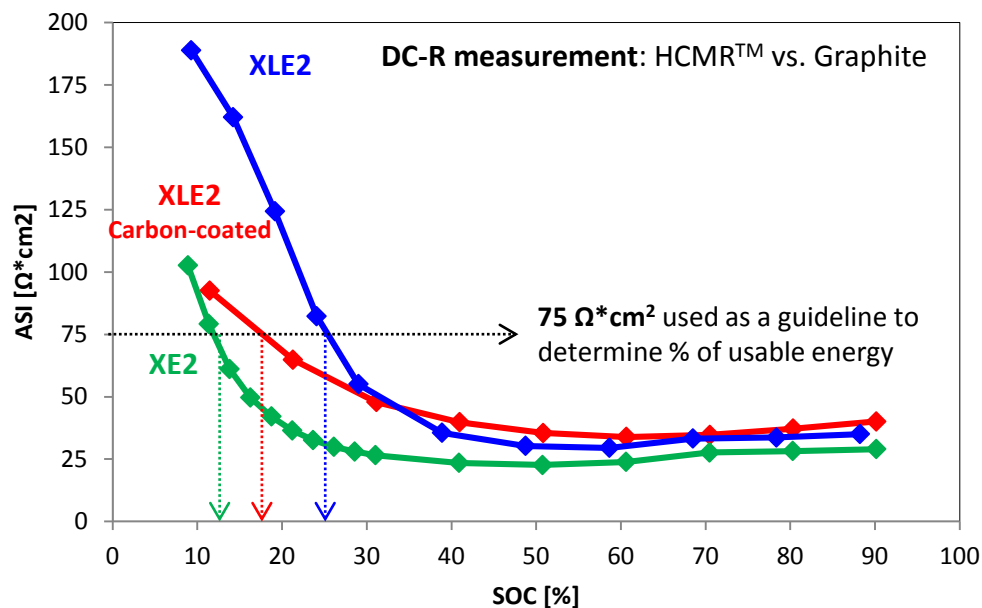
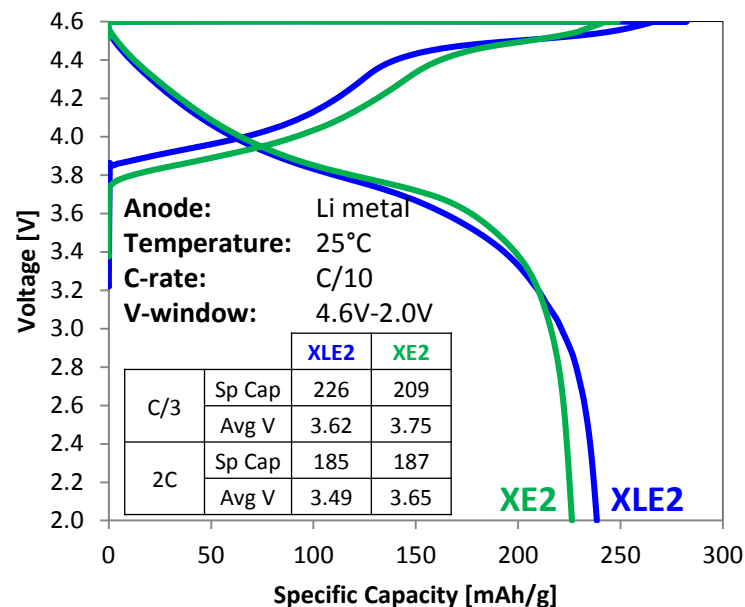
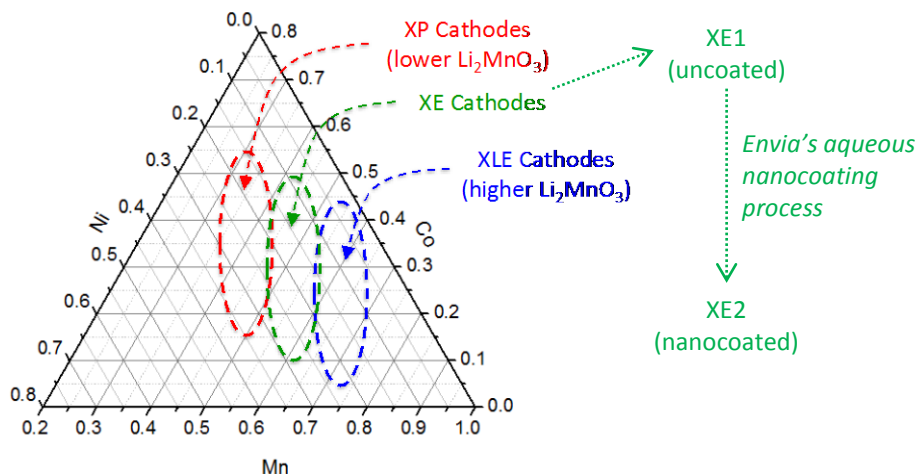
Task	Sub Tasks	Timeline										
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11
Cathode Development	1. Composition Engineering	◆(XLE)				◆(XE)						
	2. Surface coating											
	i. LiPON											
	ii. ALD											
	iii. Polymer											
	iv. Carbon											
	3. Atomistic Modeling											
	4. Diagnostic studies											
Anode Development	1. Composition Engineering											
	2. Binder Development											
Cell Development	1. Cell Sizing Studies											
	2. Electrochemical Modeling											
	3. 1~50 Ah Cell Builds (Internal)											
	4. 1~50 Ah Final Cell Build											

# Surface Modification on HCMR™-XLE Cathode



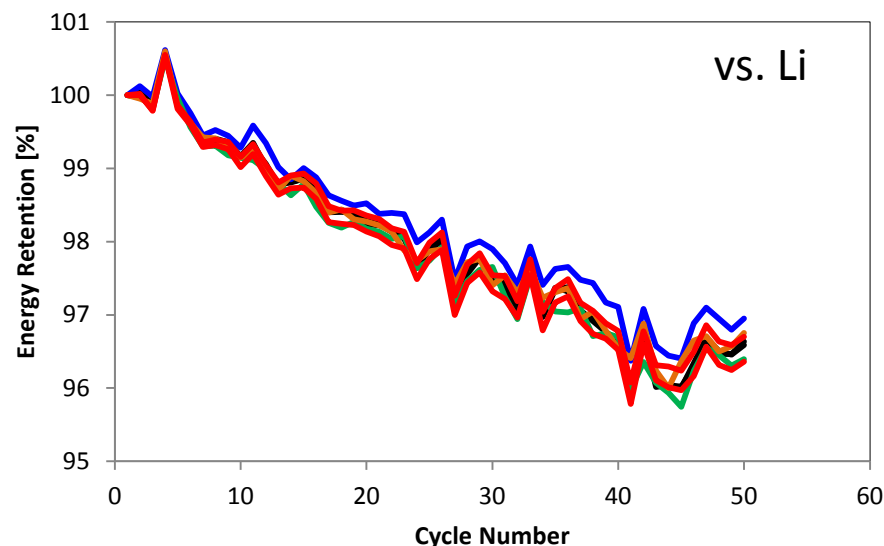
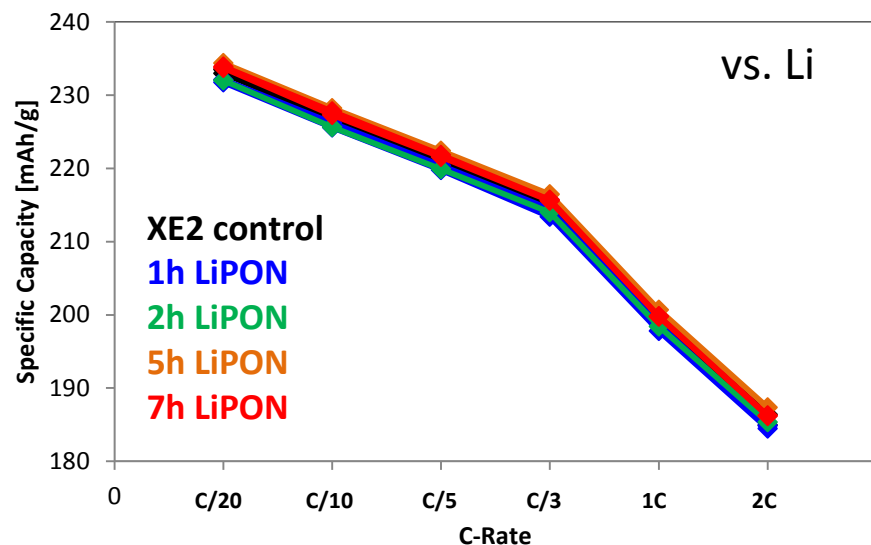
LiPON,  $\text{Al}_2\text{O}_3$  (via ALD), and polymer (PEDOT:PSS) coatings on HCMR™-XLE did not prevent loss of usable energy

# Compositional Engineering



PHEV cells demand high power – The newly developed composition HCMR™-XE is better or on-par in capacity at high rates with higher average voltage than HCMR™-XLE material.

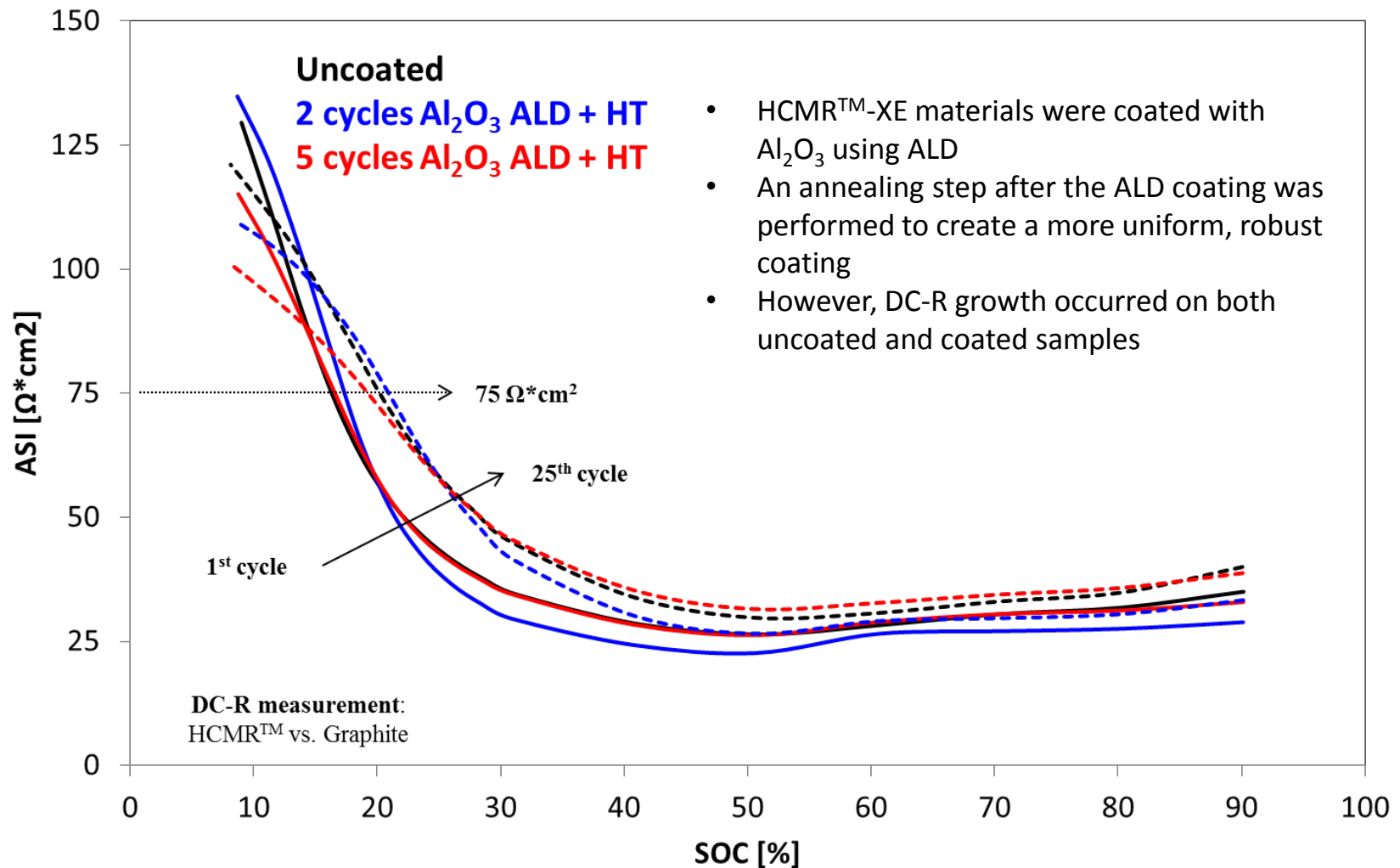
# LiPON-Coated XE2: Electrochemical Properties



- LiPON coated XE2 materials perform nearly identically to uncoated
- No improvement in capacity and average voltage – signifies no effective enhancement in DC-R

LiPON coating does not improve rate-capability nor cycle-life.  
Negative impact on Average Voltage at faster rates.

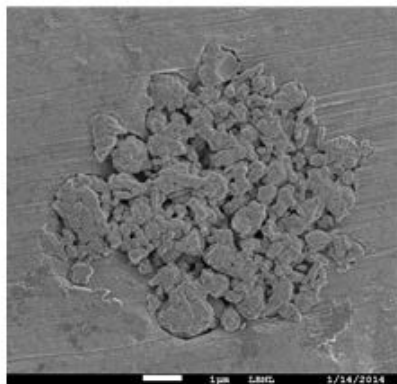
# ALD-Coated XE2: Electrochemical Properties



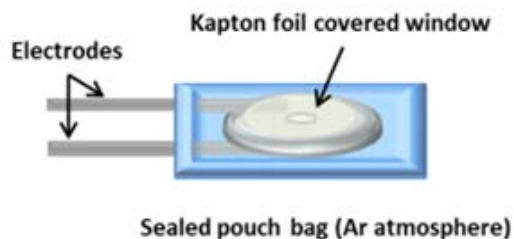
HCMR™-XE ALD coating studies with High Temperature treatment did not prevent DC-R growth after 25 cycles

# Diagnostics Studies

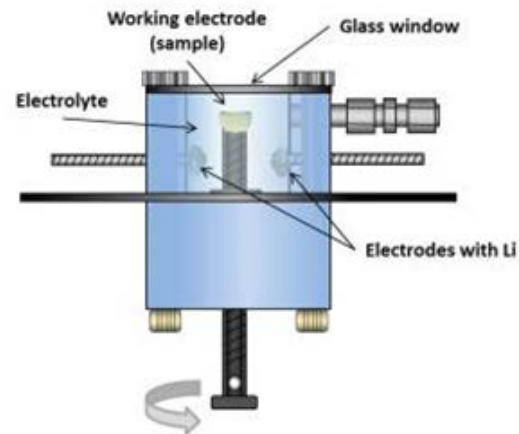
Section of model  
electrode



*In situ* XRD cell



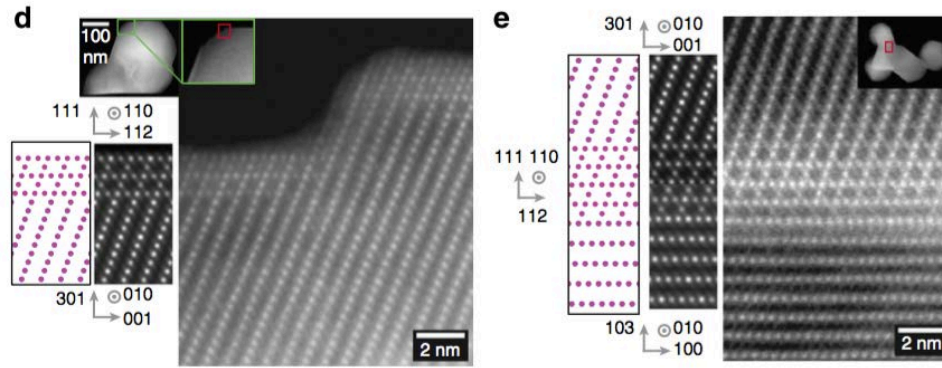
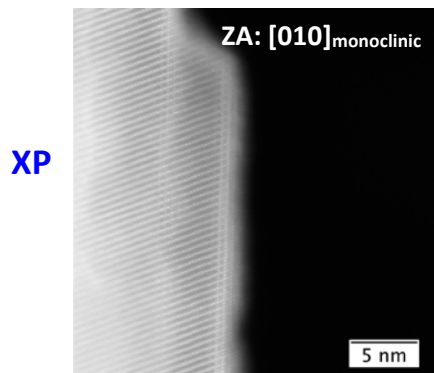
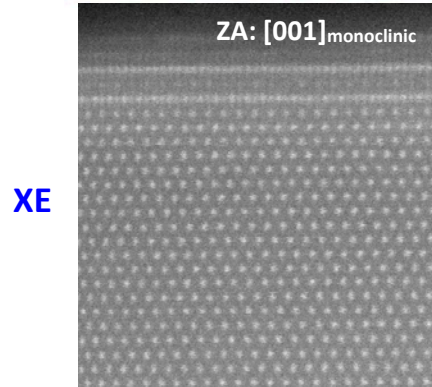
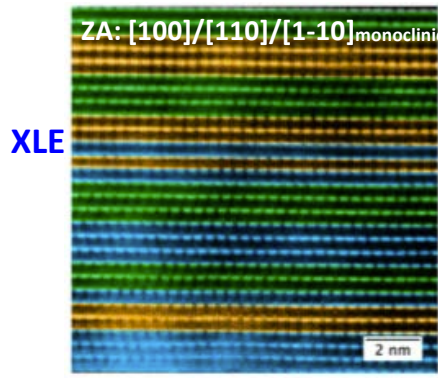
*In situ* Raman cell



STEM – Microscopic Analysis @ NCEM  
& Super STEM, UK



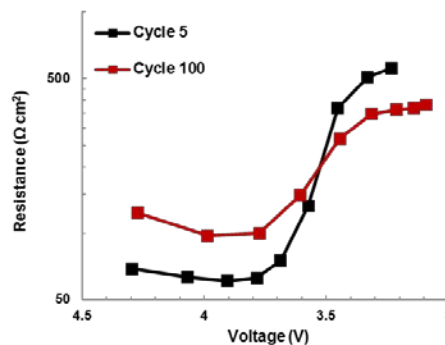
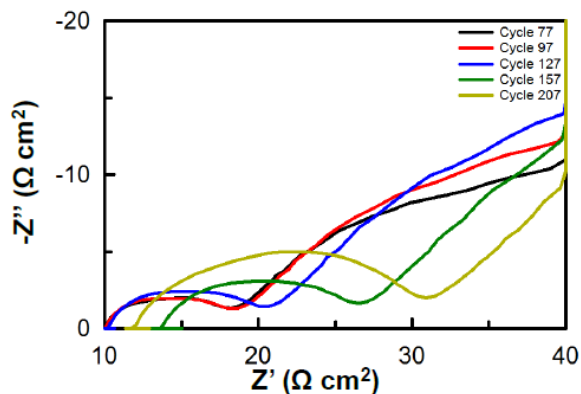
# Study of Structure Using HAADF STEM imaging



A. K. Shukla et al. Nat Commun, vol. 6, p. 8711, Oct. 2015

- Bulk structure: Preliminary results obtained from HAADF STEM analysis of XLE, XE and XP materials suggests that as Li and Mn content is decreased, there is an increase in variation of lithium content in the shared column present in monoclinic domains as observed from  $[100]$  monoclinic zone axis.
- Surface structure: All three materials exhibited the presence of spinel surface having the same orientation relationship with the bulk structure and also with similar thickness ( $\sim 2$  nm).
- The results indicate that the composition does not have an effect on the thickness of this spinel layer, indicating that the bulk structure might be more responsible in the reduction of DC-R with decrease in Li/M ratio.

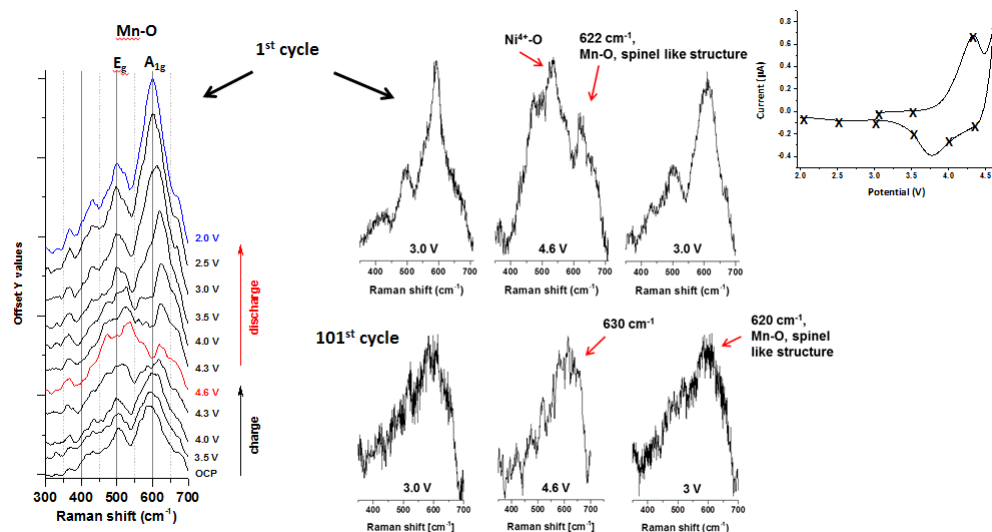
# Diagnostics – Spectroscopy & Electrochemical



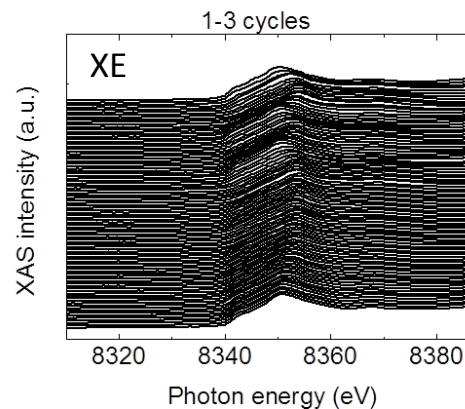
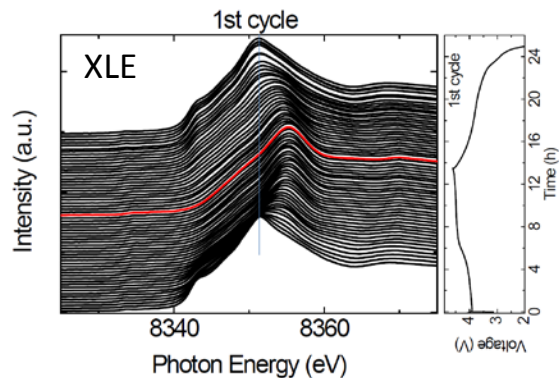
- EIS studies show increase in surface film thickness mainly due to loss in particle contact.
- EC analysis of HCMR™-XE and HCMR™-XLE cathodes show that DC-R is caused by surface film buildup at lower states of charge
- Cathode material diffusivity changes due to changes in the lattice parameter during a single cycle.

- Li<sup>+</sup> diffusivity changes dramatic below 3.8 V within a cycle
- No change of Li<sup>+</sup> diffusivity in HCMR™ material with prolonged cycling

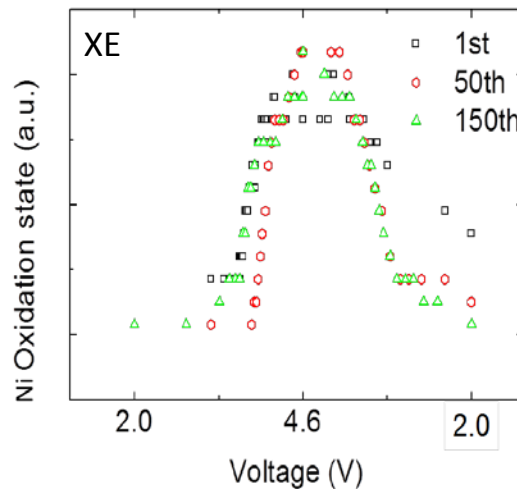
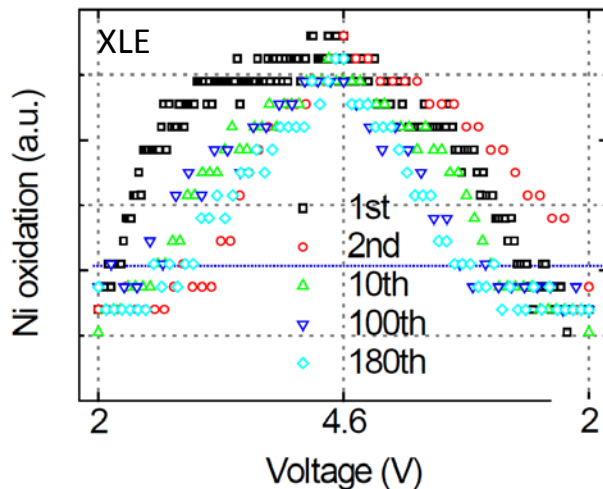
- Surface changes to a spinel like structure. Changes in surface transition metal activity.
- Ni<sup>4+</sup>/Ni<sup>2+</sup> redox reactions observed during 1st cycle
- No Ni<sup>4+</sup>/Ni<sup>2+</sup> redox reactions observed after 100 cycles



# NE-XANES – HCMR™ XLE vs. XE



- XANES is an attractive technique to compute the average oxidation number of transition metals as a function of (1) applied voltage and (2) cycle number

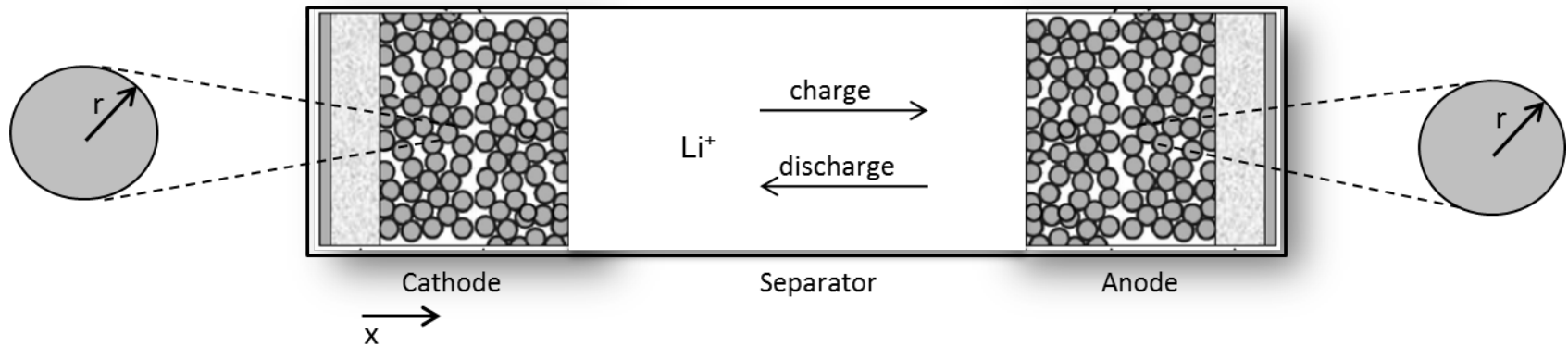


- Change in Ni oxidation number from 2+ to 4+ when charging the cell to 4.6V
- Behavior at each cycle is more stable for the HCMR™-XE2 material than HCMR™-XLE2.

HCMR™-XE2 cathode shows less irreversibility with respect to Ni oxidation number profile compared to HCMR™-XLE2.

# Electrochemical Modeling

Schematic of a single unit cell



- Pseudo-2D model accounting for variation in the field variables along the thickness of the unit cell
- Base model accounts for potential gradients in solid and liquid (Ohm's law), concentration gradients in solid and liquid (Fick's law), and intercalation reaction (Butler-Volmer kinetics)

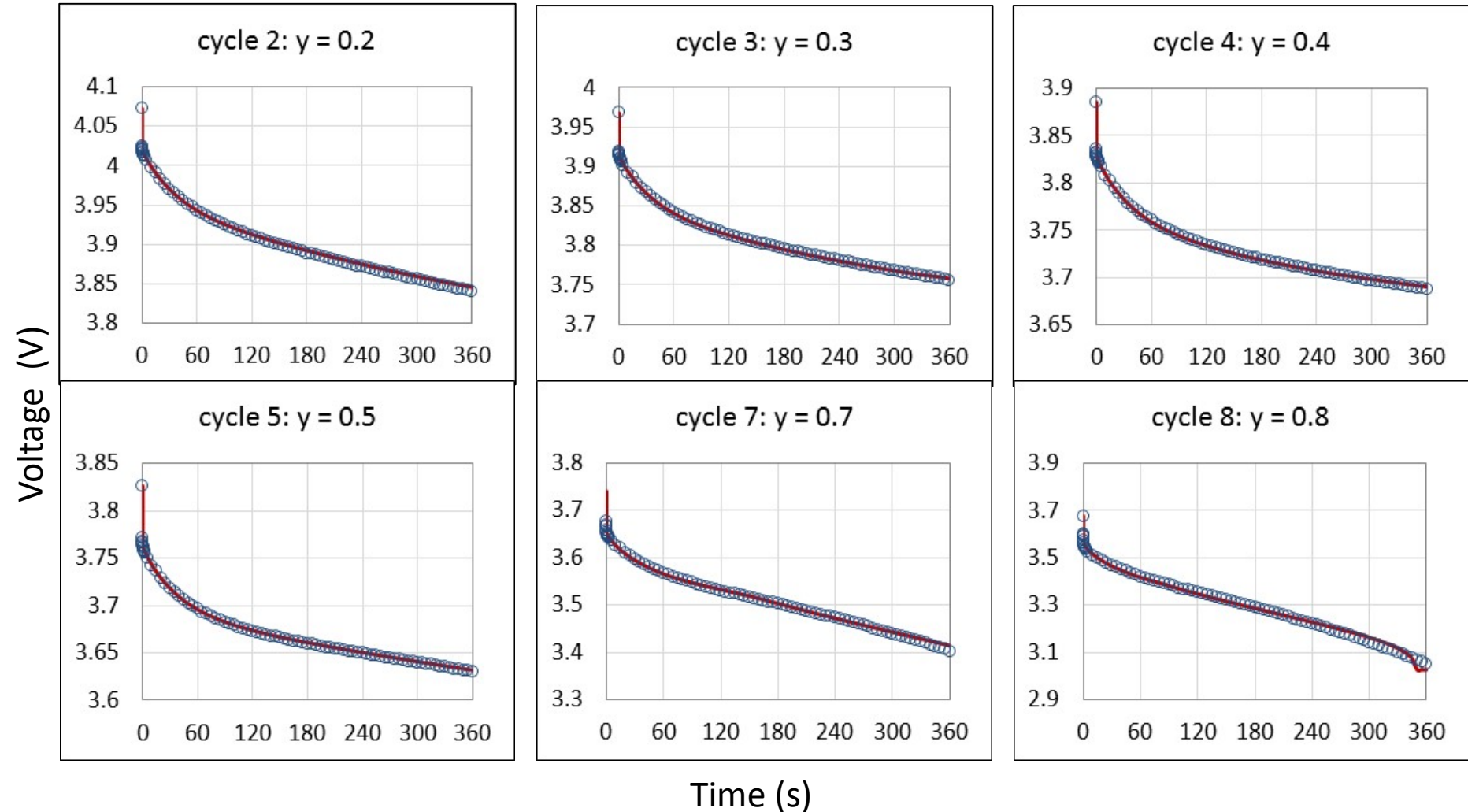
## Model Inputs

- Cell design parameters
- Electrolyte properties from literature
- Fitted parameters:
  - Solid state diffusivity
  - SEI film resistance
  - Reaction kinetics
  - Electrode tortuosity

# Electrochemical Model Fit (HCMR™ XE1)

Half cell voltage as a function of time

Symbols: data  
Line: model



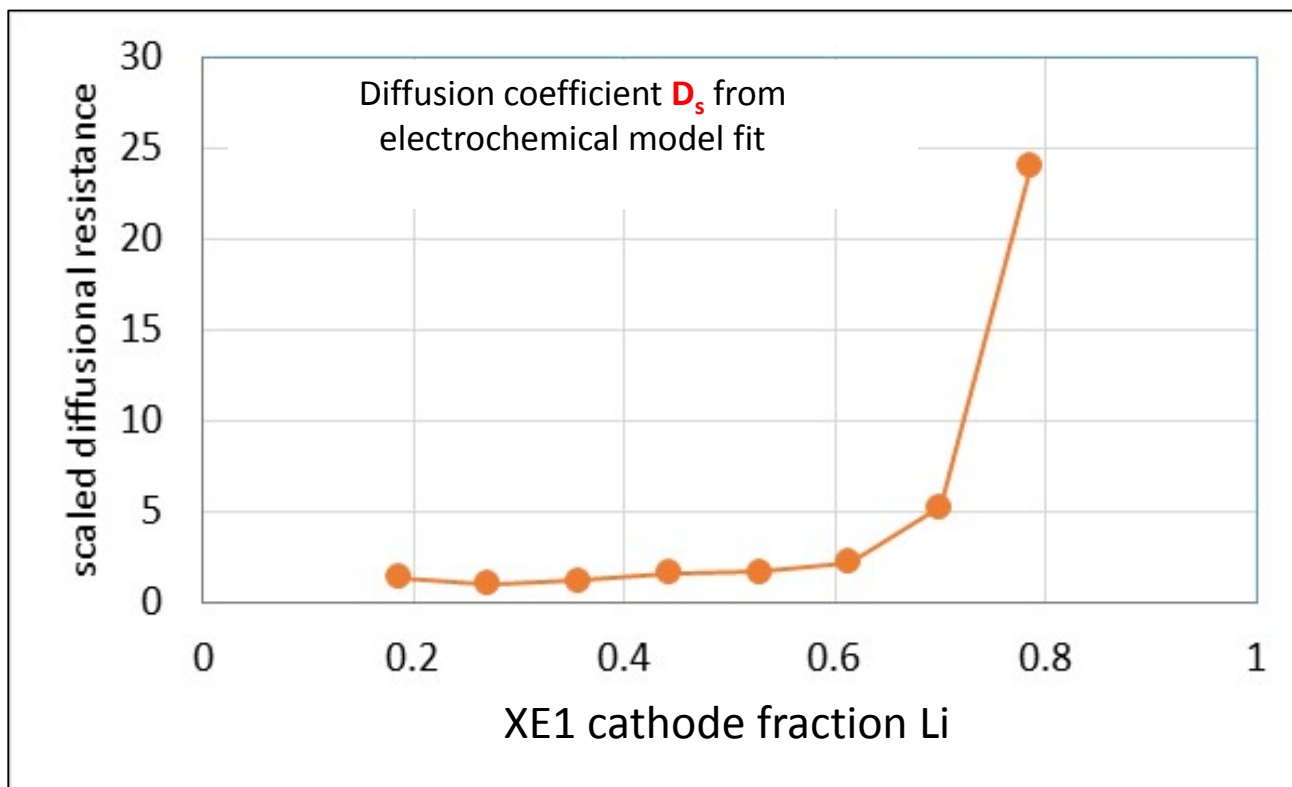
Good agreement between model and experiment

# Solid-State Diffusional Resistance

$$R_d = \frac{r_p^2}{3 F L \varepsilon_s C_{smax} D_s} \left( -\frac{dU}{dy} \right)$$

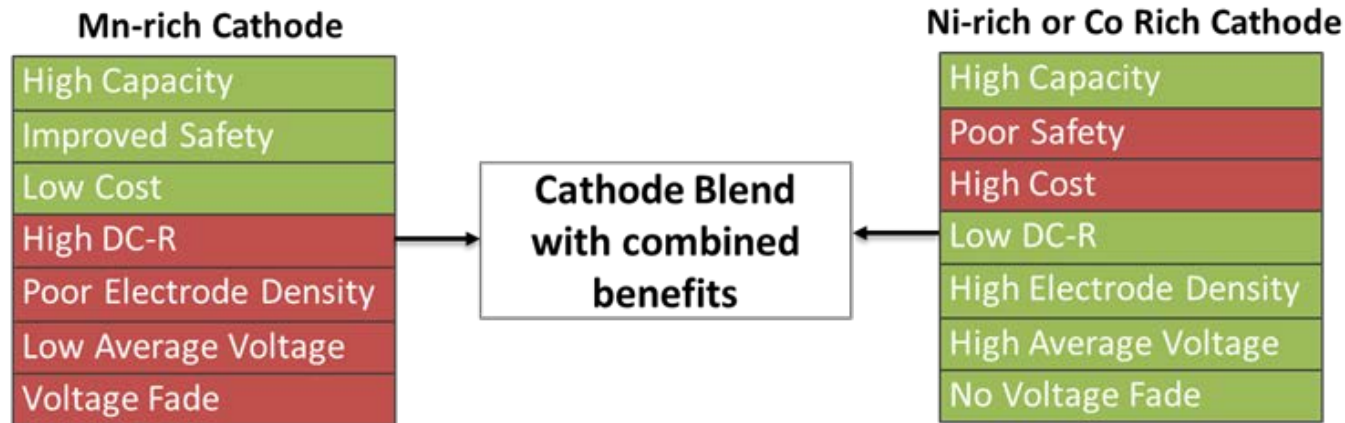
Daniel Baker and Mark Verbrugge, Journal of the Electrochemical Society, **160** (8), A1319-A1332 (2013)

Particle diffusional resistance trend similar to DC-R, mainly responsible for increased DC-R at low SOC (high Li fraction)



# Cathode Blends

Goal: Achieving 200 Wh/kg without using the high voltage capacity from HCMR™-XE



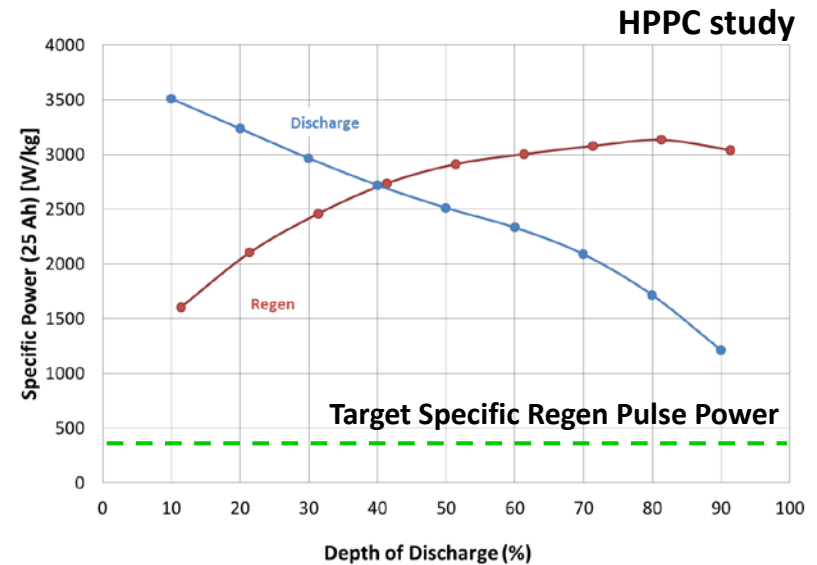
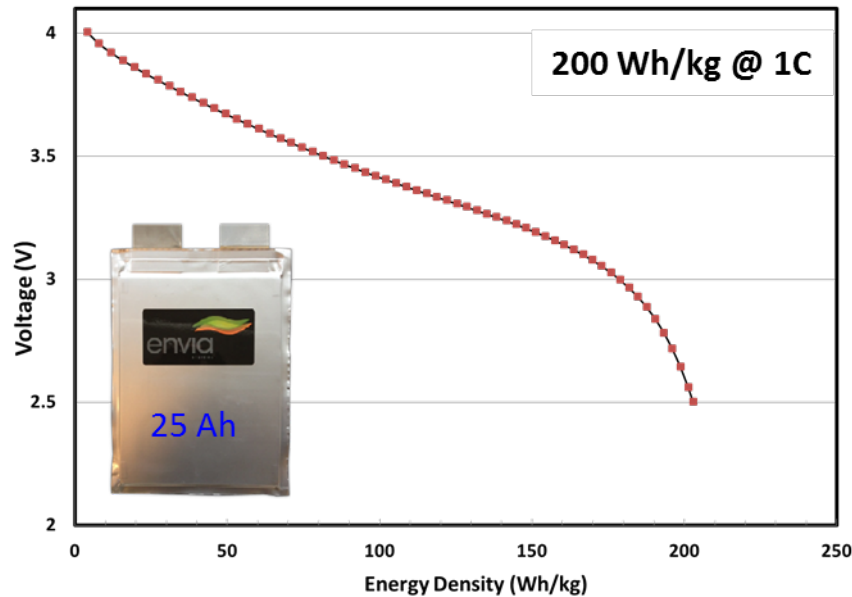
HCMR™-XE exhibits low DC-R compared to HCMR™-XLE. However, the phase stability or loss of power (increase in DC-R) with cycling is inevitable even in HCMR™-XE if operated at higher charge voltages (>4.3V).

Blending HCMR™-XE with other cathode materials benefits with higher active, higher loading in the electrode. This will enable a cell design which allows cell operation at lower charge voltages.

HCMR™-XE structure is maintained showing NO voltage fade (no phase change) when operated in limited upper cut-off window.

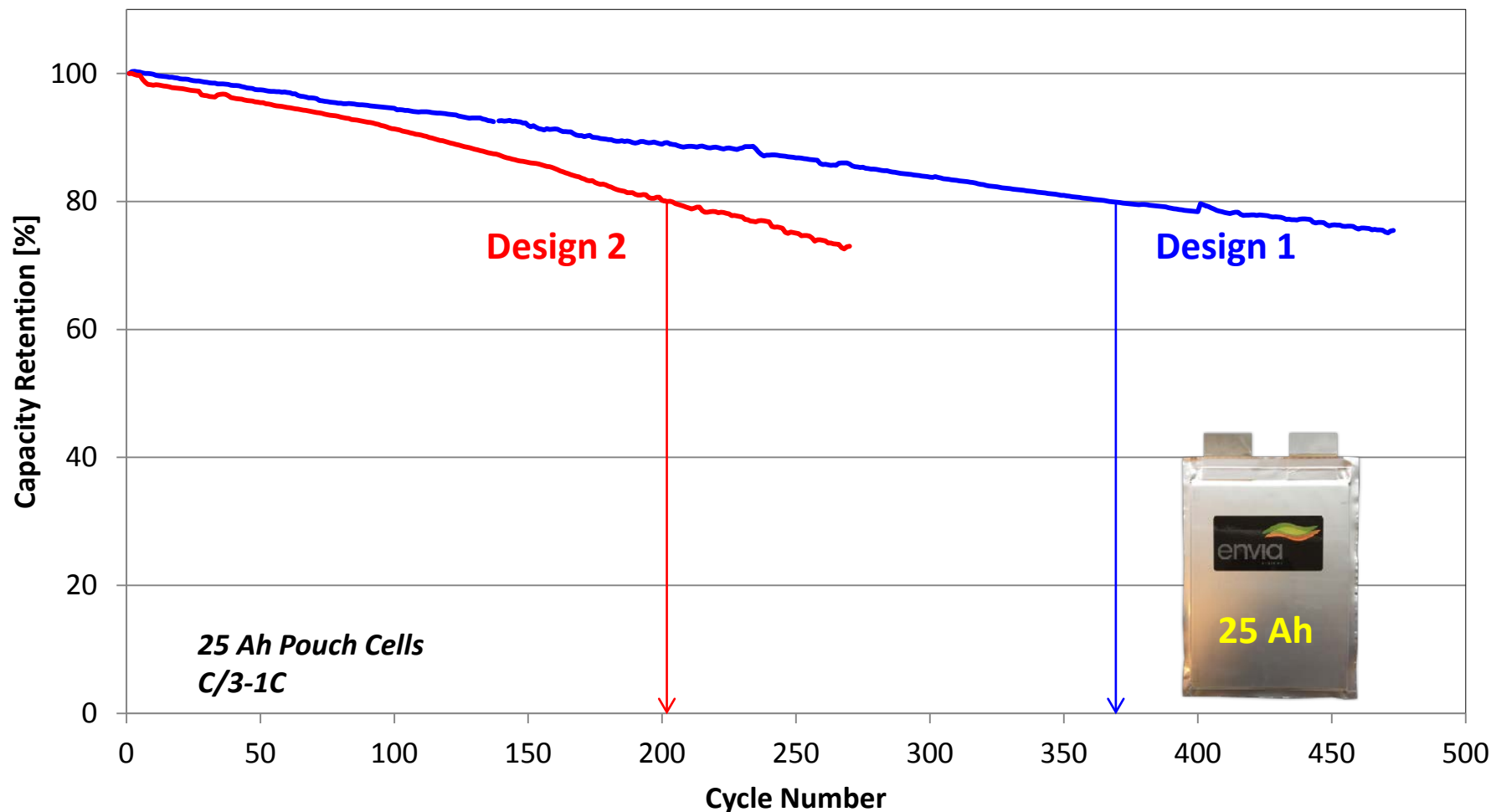
Various cathode and anode blends were formulated to meet the ABR cell metrics and cells with the best performing cell design were chosen for the final ABR cell deliverable to INL.

# Design 1 – Energy Density and HPPC



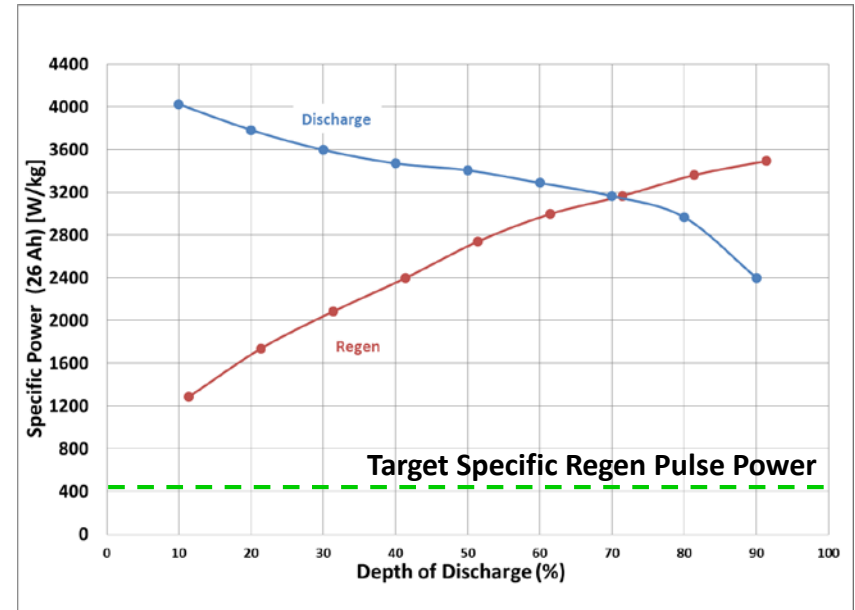
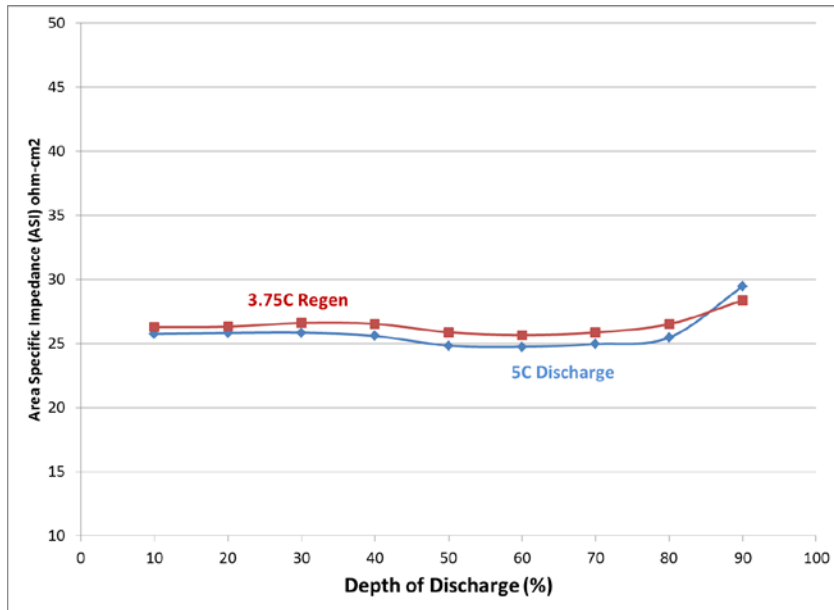
Chracteristics	Unit	PHEV40 ABR Targets	XE Cell after RPT0
			Design 1
Specific Discharge Pulse Power	W/kg	800	1718
Discharge Pulse Power Density	W/L	1600	3693
Specific Regen Pulse Power	W/kg	430	2103
Regen Pulse Power density	W/L	860	4523
Specific Energy @ 1C	Wh/kg	200	203
Energy Density @ 1C	Wh/L	400	436
Calendar Life	Years	10+	TBD
Cycle Life (C/3 ~ 1C)		5000	350
Operating Temperature	°C	(-30 ~ +52)	25 °C

# Designs 1 & 2 – Cycling Performance



- Met 200 Wh/kg with Designs 1 and 2
- Design 2 has poor cycle-life compared to Design 1
- Design 2 anode has higher Carbon content, but the binder was not optimized for this formulation

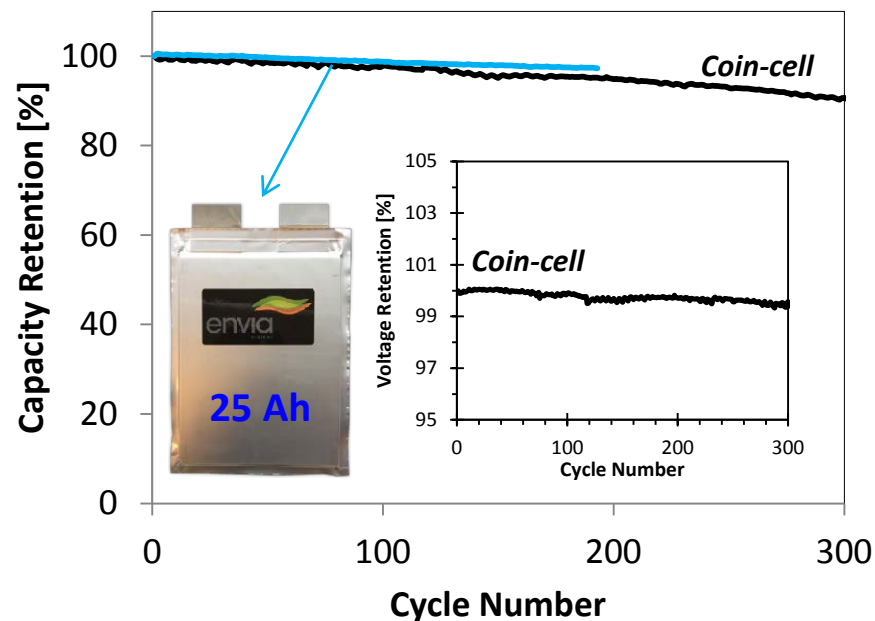
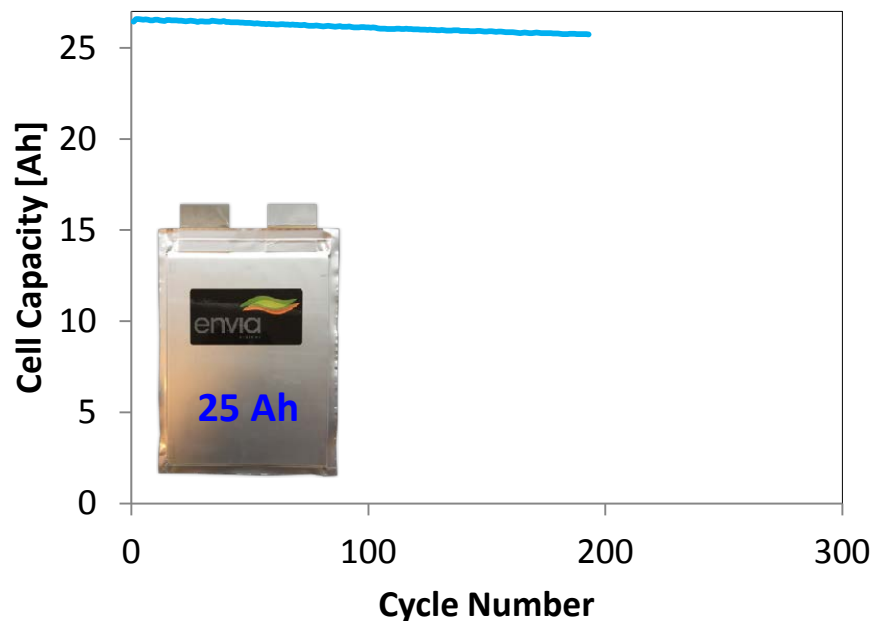
# Design 4 – HPPC for 26 Ah Cell



Characteristics	Unit	PHEV40 ABR Targets	XE Blend: Si-Gr Cells	
			Design 1	Design 4
Specific Discharge Pulse Power	W/kg	800	1718	2966
Discharge Pulse Power Density	W/L	1600	3693	6701
Specific Regen Pulse Power	W/kg	430	2103	1739
Regen Pulse Power density	W/L	860	4523	3930
Specific Energy @ 1C	Wh/kg	200	203	210
Energy Density @ 1C	Wh/L	400	436	474
Calendar Life	Years	10+	TBD	TBD
Cycle Life (C/3 ~ 1C)		5000	350	TBD
Operating Temperature	°C	(-30 ~ +52)	25 °C	25 °C

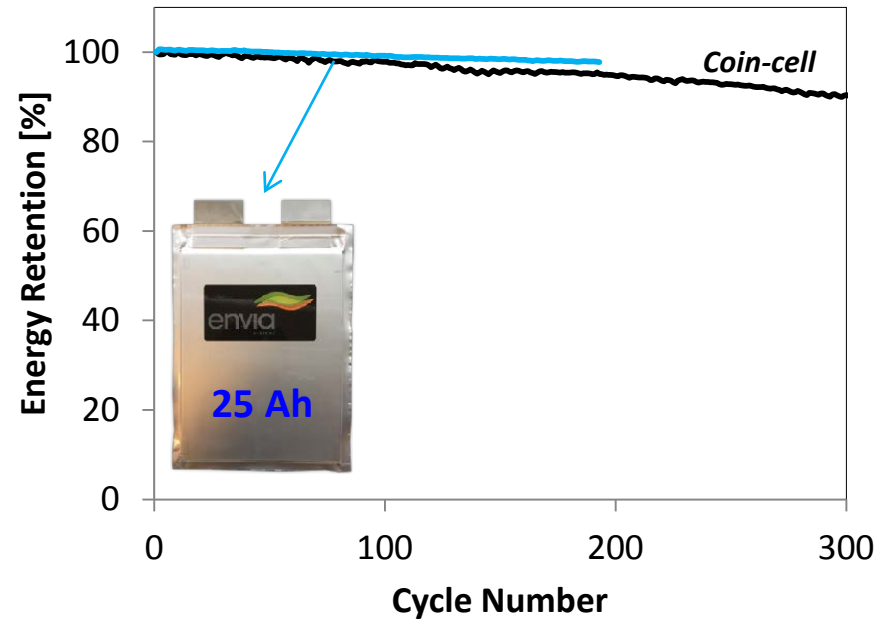
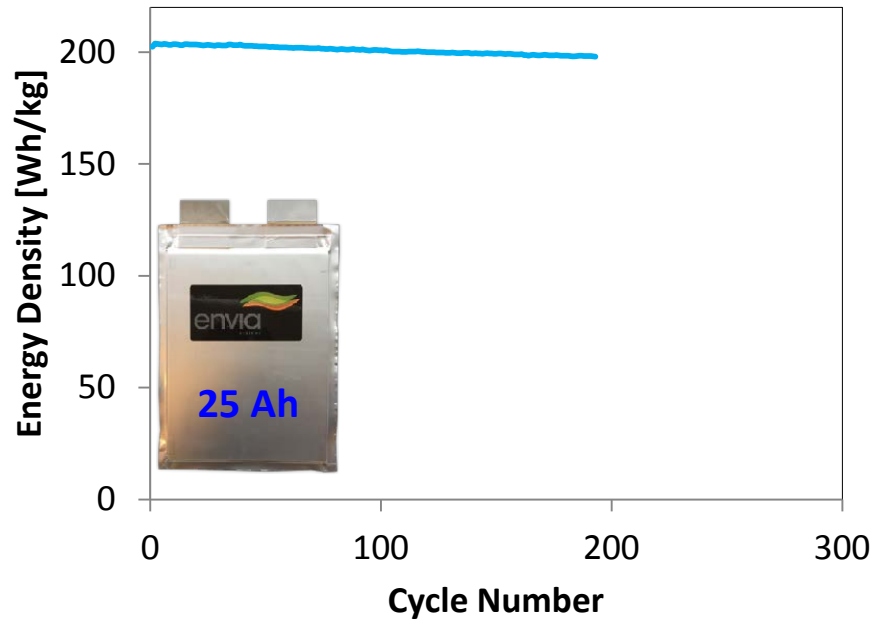


# Design 4 – Cycling Performance (1)



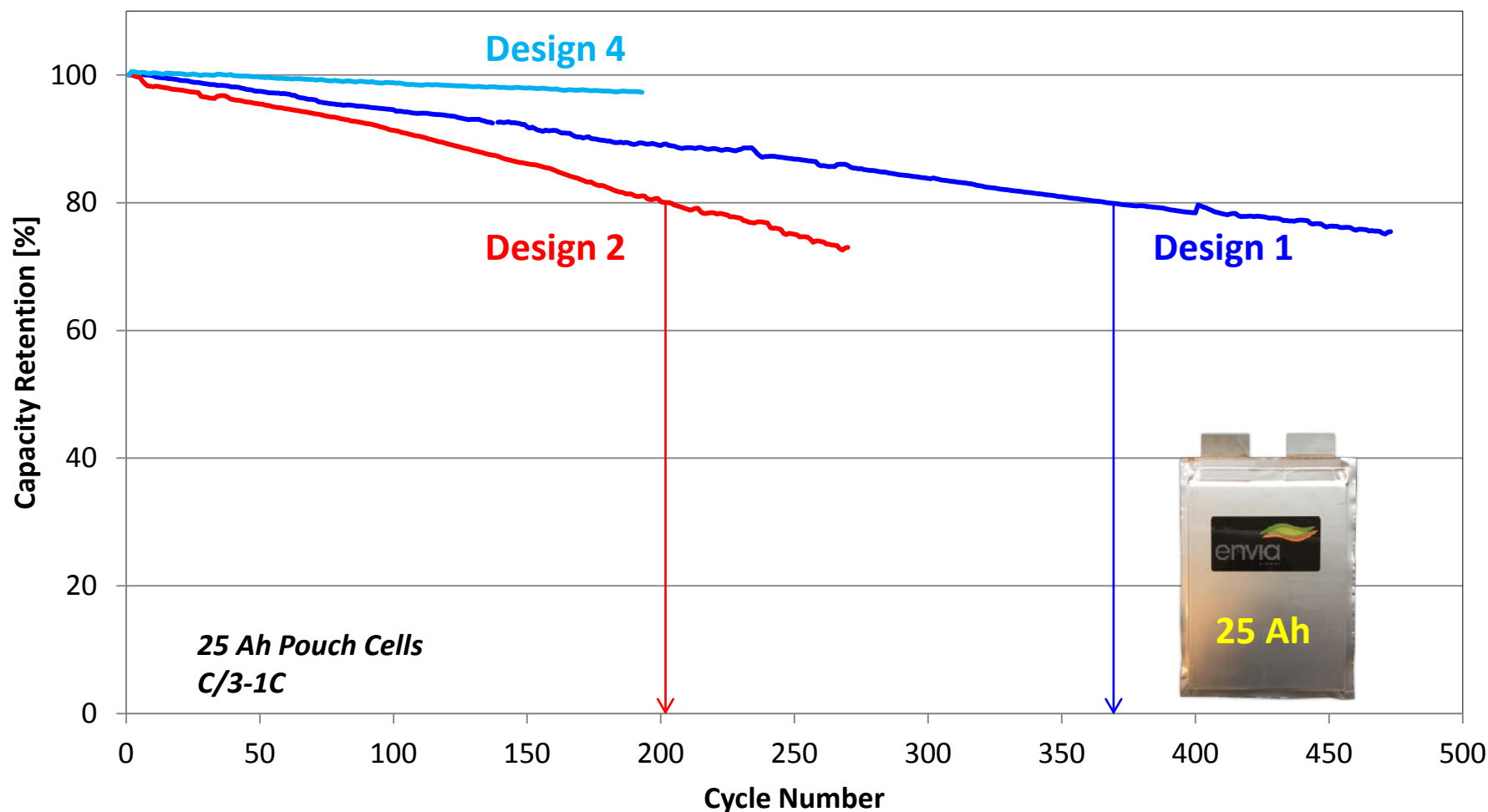
- Design 4, 25 Ah format cell shows capacity retention >97% after ~190 cycles
- Design 4, 25 Ah format cell is surpassing the analogous Design 4 tested in coin-cell format
- Voltage retention remains >99% after 300 cycles in the coin-cell, suggesting no phase-change taking place in the cathode material

# Design 4 – Cycling Performance (2)



- Design 4, 25 Ah format cell shows energy retention >97% after ~190 cycles
- Design 4, 25 Ah format cell is surpassing the analogous Design 4 tested in coin-cell format

# Cycling Performance of Cell Deliverables



- Met 200 Wh/kg @ 1C with Designs 1, 2, and 4
- Design 4 has optimized anode formulation, showing the best cycle ability so far

# Conclusions

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- HCMR™-XLE cathode showed high capacity, yet very high DC-R which leads to poor power characteristics.
- HCMR™-XLE also showed large increase in resistance with cycling leading to further loss in usable energy.
- Different nanocoatings on HCMR™-XLE such as  $\text{Al}_2\text{O}_3$ , LiPON, polymer etc. via different chemical and physical deposition methods did not reduce DC-R nor did they prevent the increase in DC-R with cycling.
- Composition engineering (from HCMR™-XLE to HCMR™-XE) provided an effective solution for the DC-R challenge for the Li-rich NMC.
- The PFM binder was not compatible with Envia's Si-based anode material resulting in deterioration of the EC characteristics of the anode.
- Cathode blends of HCMR™-XE with Ni-rich or Co-rich cathode materials were developed to operate the cell in the optimized voltage window in order prevent any phase-change driven energy loss with cycling.
- 26 Ah cells were built meeting ABR cell targets of 200 Wh/kg and 400 Wh/L without exposing the cathode to deteriorating voltages.

# Acknowledgements

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